

TAB A
TO EXHIBIT 14

IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF DELAWARE

CRYOVAC, INC.,
Plaintiff and Counter-Defendant,

v.

PECHINEY PLASTIC PACKAGING, INC.,
Defendant and Counter-Plaintiff.

Civil Action No. 04-1278

Hon. Kent A. Jordan

Declaration of Seymour G. Gilbert

I, Seymour G. Gilbert, declare as follows:

1. I received my B.S. degree in 1935, M.S. degree in 1938, and Ph.D. in 1941 from Rutgers University.
2. I worked at Pabst Company as a Research Chemist from 1951-1958.
3. I began as a principal scientist at Milprint, Inc. in 1958 and left in 1965 as the Corporate Technical Director.
4. I served as Professor of the Food Science Department at Rutgers University from 1965-1988.
5. I served as Deputy Director of the Packaging Science and Engineering Program in the Engineering School at Rutgers University from 1988-1998.
6. I have patents on packaging films, as well as, other areas. My 200 publications include work on polymers and their uses, including multilayer films. I consulted, designed and produced the food packaging multilayer films used on the Apollo project.
7. I have conducted several studies for Allied Chemicals since coming to Rutgers in 1965. I developed special tests for evaluating packaging materials, starting at Milprint, and made such studies and major research studies after coming to Rutgers with regular publication of research findings. By agreement with Allied, the results of the studies which began in 1981 were to be published. The film samples and financial aid were provided by Allied. There were two studies for Allied.

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER
PPPI 013828

DTX0690

8. The first study for Allied was completed by 1982 and its results were described in at least: 1) the article "Study of Barrier Properties of Polymeric Films to Various Organic Aromatic Vapors" by S.G. Gilbert, E. Hatzidimitriu, C. Lai and N. Passy in the 1983 Edition of Instrumental Analysis of Foods Recent Progress Volume 1; and 2) the article "Environmental and Material Composition Effects on Film Permeability as Related to Meat Packaging" by Seymour G. Gilbert, Grace R. Huang-Lai and Christopher C. Lai presented at the 36th Annual Reciprocal Meat Conference held on June 12-15, 1983.

9. The second study for Allied commenced around 1983 and included a film having the structure HDPE/TIE/NYLON/EVOH/NYLON/TIE/HDPE. I received all the films of the second study for Allied at the same time. The second study for Allied was described in at least: 1) the article "Nylon Film Effective Packaging" in the December 14, 1984 Journal of Commerce ("Journal of Commerce Article"); 2) the Allied Engineered Plastics News Release "Rutgers Study Confirms Nylon Barrier Properties for Food and Other Sensitive Packaging" ("Allied News Release"); and 3) the article "Odor Barrier Properties of Multi-Layer Packaging Films at Different Relative Humidities" by E. Hatzidimitriu, S.G. Gilbert and G. Loukakis in the March-April 1997 issue of Journal of Food Science ("Journal of Food Science Article").

10. I agree with the Allied News Release that the films of the second study for Allied were coextruded.

11. The Journal of Commerce Article disclosed nylon and EVOH used together in film structures. The first study did not include a film with nylon and EVOH used together in film structures. Only the second study included a film with nylon and EVOH used together in film structures. Therefore, the study described in the Journal of Commerce Article as "Rutgers is currently conducting additional testing for Allied" is the second study for Allied.

12. The objectives of these two studies for Allied were to determine the physical and chemical properties of film for food packaging, principally, water, gas and odor contaminant permeabilities, and physical endurance during fabrication and its long use.

13. Two main protocols were used for these two studies for Allied. The first

was for physical properties which uses a preliminary conditioning under various environmental stress conditions of temperature and humidity followed by a severe physical stressing. We used an apparatus developed by Gelbo which used the cylindrical test films suspended between two mandrels and a motor which applied both rotation and twisting to severely stress both machine and transverse directions as related to the manufacturing process. The test is particularly useful in multilayer films held together by tie layers as it applies stress to the structure as might be applied during package formation and shipping.

14. One of the factors for such properties is crystallinity and the degree of orientation of the various polymers used. All of the films supplied were tested independently prior to use at Rutgers for identifying physical and chemical properties prior to experimental use. This is done to ensure identity and to help interpret the results of sample films.

15. The methods include physical tests such as: 1) Instron Tester, which provides stress data relating to orientation; 2) Cross Polarization to visualize orientation; 3) infrared tests to identify the various components of multilayer film including its chemical composition and thickness; and 4) special gas and organic vapor permeability for barrier properties by test methods developed at my laboratory known as the Gilbert-Pegaz tester.

16. It is my recollection that results of the Instron Tester and the Cross Polarization tester showed that the 1.4 mil HDPE/TIE/NYLON/EVOH/NYLON/TIE/HDPE film, identified as Film C in the Journal of Food Science Article, was oriented.

17. It is my recollection that the infrared spectra obtained from the individual layers of the 1.4 mil HDPE/TIE/NYLON/EVOH/NYLON/TIE/HDPE film, identified as Film C in the Journal of Food Science Article, did not show any obvious differences in either composition or thickness of the corresponding layers around the center. Such differences would have been noted in our publications.

18. The permeation rates for Film C, as disclosed in Tables 2 and 3 of the Journal of Food Science Article, are consistent with the permeation rates of an oriented multilayer film exhibiting high barrier properties.

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

19. I was retained by Pechiney Plastic Packaging, Inc. as a consulting expert.

I have consulted on matters other than the studies for Allied Chemicals.

I declare under penalty of perjury that the foregoing is true and correct.

Date: August __, 2005

Seymour G. Gilbert

was for physical properties which was a preliminary concerning, under various environmental stress conditions of temperature and humidity followed by a severe physical testing. We used an apparatus developed by Orlon which used the cylindrical test film suspended between two clamps and a motor which applied both tension and twisting to severely stress both machine and transverse directions as related to the manufacturing process. The test in particular would be multilayer films held together by the layers as it applies stress to the structure as might be applied during package formation and shipping.

14. One of the factors for such properties is crystallinity and the degree of orientation of the various polymers used. All of the films supplied were tested independently prior to use at Rutgers for identifying physical and chemical properties prior to experimental use. This is done to ensure identity and to help interpret the results of sample films.

15. The various initial physical tests such as: 1) Inverse Tensile, which provides stress data relating to orientation; 2) Cross Polarization to determine orientation; 3) Infrared tests to identify the various components of multilayer film including its chemical composition and thickness; and 4) special gas and organic vapor permeability for barrier properties by the methods described in my Barrier Properties in the Food Packaging Industry.

16. It is my recollection that the results of the Inverse Tensile and the Cross Polarization tests showed that the 1.4 mil EKV/TEANTLONEVOMNYLON/TEHDE film, identified as Film C in the Journal of Food Science Article, was oriented.

17. It is my recollection that the infrared spectra obtained from the individual layers of the 1.4 mil EKV/TEANTLONEVOMNYLON/TEHDE film, identified as Film C in the Journal of Food Science Article, did not show any obvious differences in either composition or thickness of the corresponding layers across the center. Such differences would have been noted in our publications.

18. The permeation rates for Film C, as discussed in Tables 2 and 3 of the Journal of Food Science Article, are consistent with the permeation rates of an oriented multilayer film exhibiting high barrier properties.

3

19. I was assisted by Precision Plastic Technology, Inc. in a laboratory setting. I have conducted no matters other than the studies for Allied Chemicals. I declare under penalty of perjury that the foregoing is true and correct.

Date: August 16, 2005

Raymond J. Helbert
Raymond J. Helbert

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

PPPI 013832

TAB B
TO EXHIBIT 14

Eldridge Mount, III CONFIDENTIAL PORTIONS (CLEARSHIELD DETAILS & EXHIBITS 21-22) SUBJECT TO THE PROTECTIVE ORDER August 4, 2005

Chicago, IL

1

IN THE UNITED STATES DISTRICT COURT

FOR THE DISTRICT OF DELAWARE

CRYOVAC, INC.,

Plaintiff/Counter-Defendant,

CERTIFIED COPY

-vs-

Civil Action

No. 04-1728-KAJ

PECHINEY PLASTIC PACKAGING, INC.,

Defendant/Counter-Plaintiff.

NOTE: PORTIONS OF TEXT DEEMED CONFIDENTIAL -

SUBJECT TO PROTECTIVE ORDER

The videotaped deposition of ELDRIDGE MOUNT, III,
called by the Plaintiff/Counter-Defendant for examination,
pursuant to notice and pursuant to the Federal Rules of
Civil Procedure for the United States District Courts pertaining
to the taking of depositions, taken before Cynthia J. Conforti,
Certified Shorthand Reporter, at One IBM Plaza, Chicago, Illinois,
commencing at the hour of 9:02 a.m. on the 4th day of August, A.D., 2005.

Henderson Legal Services
(202) 220-4158

Eldridge Mount, III CONFIDENTIAL PORTIONS (CLEARSHIELD DETAILS & EXHIBITS 21-22) SUBJECT TO THE PROTECTIVE ORDER August 4, 2005

Chicago, IL

183

1 MR. FUCHS: Okay. Why don't we change the
2 tape.

3 THE VIDEOGRAPHER: End of tape number
4 three. Off the record at 1:46 p.m. 01:46PM

5 (Whereupon a recess was had.)

6 THE VIDEOGRAPHER: Beginning of tape
7 number four. On the record at 1:53 p.m.

8 BY MR. FUCHS:

9 Q. Did the Hatley article or the Journal of 01:54PM
10 Commerce article provide any specific disclosure
11 as to how to orient a seven-layer coextruded film?

12 A. I don't believe that they have a recipe
13 for orientation or orientation conditions.

14 Q. Okay. Will you turn to Table 1 of the 01:54PM
15 Exhibit 10.

16 A. Okay.

17 Q. Do you have that in front of you? And you
18 see at the bottom there's a film key and then a
19 description of films A, B, C, D, E, F, G, H and I.
20 You see that?

21 A. Um-hmm. Excuse me.

22 Q. And film F is indicated as being oriented,

TAB C
TO EXHIBIT 14

News Release



Engineered
Plastics

Allied Corporation
P.O. Box 2332R
Morristown, NJ 07950

For further information:

Contact Earl Hatley
(201) 455-5407

For Immediate Release

RUTGERS STUDY CONFIRMS NYLON BARRIER PROPERTIES FOR FOOD AND OTHER SENSITIVE PACKAGING

Nylon film coextrusions offer the most cost-effective barrier for flavors, aromas, and odors for food and other sensitive packaging according to the results of a scientific study undertaken by Rutgers University for Allied Engineered Plastics.

The research project, directed by Dr. Seymour Gilbert, head of the Rutgers University Food Science Department, was the second such investigation commissioned by Allied.

Results from the first study, completed three years ago, also demonstrated nylon's cost-effective barrier properties. In that initial research, film materials tested included polyvinylidene chloride (PVDC), ethyl vinyl alcohol (EVOH), and glassine as well as nylon. Films with thin nylon cores proved to have the broadest range of performance properties with optimum flavor aroma barrier. Only EVOH offered better permeation resistance to acetic acid, ethyl acetate, and toluene, although the nylon films provided acceptable permeation resistance at a cost approximately half that of EVOH.

The second research project sought to determine whether nylon and EVOH in a single specification have a synergistic effect on flavor and aroma which would be cost-effective; and to test other film structures with additional permeants which have a broader range in simulating various flavors and aromas used in

-more-

PPPI 008492

DTX0127

-2-

food, medical, and industrial packaging. Where the first study tested film only at zero percent relative humidity, the present investigation would be conducted under conditions of zero and 80 percent humidity; to date, the only results available from the second study are of film structures tested at zero percent humidity.

Dr. Gilbert, who designed the test cell in which the permeation rates were measured, subjected eight different coextruded film structures to nine different permeants. Film samples were clamped in the permeation cell and test compounds in concentration of 100 ppm were introduced to chambers within the cell. Concentration of test compounds in the chambers were measured by gas chromatograph to determine permeation rate of the compounds.

Permeants selected for the tests were methyl ethyl ketone, ethyl acetate, toluene, (all solvents), methyl salicylate, ethyl phenol acetate, limolene, beta-pinene, styrene, and menthol. These include compounds found in breath fresheners, soaps, and other products, flavorants, and permeants used to simulate hydrocarbons, undesirable packaging compounds, and organic compounds used in medicinal packaging.

The findings are particularly important to packagers of shelf stable foods such as packaged baked goods, candies, confections, flavor enhanced cereals, cakes, and snack foods.

Combinations of nylon and EVOH do not, Dr. Gilbert's tests showed, produce a significant synergistic effect in terms of barrier properties compared to a nylon-only coextrusion or an EVOH-only coextrusion.

-more-

PPPI 008493

-3-

In addition, according to test results, the nylon-only coextrusion, or the modified-nylon coextrusion, showed excellent barrier properties for all permeants compared to a PETG coextrusion and a PVDC-coated oriented polypropylene film.

Nylon also offers excellent resistance to grease and oil, and high-temperature performance as well as impact-, puncture-, and tear-resistant properties.

For detailed findings of the second Rutgers study, see the attached tables for measured permeation for all film structures with all tested permeants, and permability ratings (Poor, Fair, Good, Excellent) based on actual laboratory measurements.

For more information, contact Earl Hatley, Product Manager, Allied Engineered Plastics, PO Box 2332R, Morristown, NJ 07960, (201) 455-5407.

PPPI 008494

Table 1
Permeability in gr/m²xdayx100 ppm at 73°F and 0.8RH

Film	Methyl Ethyl Ketone	Ethyl Acetate	Methyl Salicylate	Ethyl Phenyl Acetate	Limonene	B-Pinene	Toluene	Styrene	Menthol
A	0.43	<0.0003	0.0046	0.0085	0.0409	0.0120	0.001	<0.0003	<0.0002
D	0.65	0.30	0.0011	<0.0060	0.0012	0.0013	0.027	0.0610	<0.0001
C	0.90	<0.0004	<0.0003	<0.0080	0.0014	<0.0004	0.002	0.0054	<0.0001
D	0.65	<0.0004	<0.0002	<0.0080	0.0018	<0.0011	0.001	<0.0003	<0.0001
E	0.77	<0.0004	<0.0002	<0.0080	<0.0003	<0.0009	0.0004	0.0005	<0.0001
F	<0.01	<0.0004	0.009	<0.0070	0.0400	0.0036	0.0003	<0.0002	<0.0002
G	2.40	6.86	2.160	0.234	0.0315	0.0008	1.310	0.0018	0.0020
H	0.44	0.52	0.071	0.016	0.0400	0.0320	0.470	0.0046	<0.0002
I	0.02	0.04	0.024	<0.0080	0.0106	<0.0012	0.005	0.0059	0.0011

FILM KEY:

- A. HDPE/TIE/NYLON/EVA
 B. HDPE/TIE/EVON/EVA
 C. HDPE/TIE/NYLON/TIE/EVON/TIE/NYLON/TIE/HDPE
 D. HDPE/TIE/MODIFIED NYLON/TIE/HDPE
 E. NYLON/EVON/NYLON/TIE/LLOPE/TIE/LLOPE
 F. (ORIENTED)PP/TIE/EVON/TIE/PP
 G. PP/TIE/PET/TIE/PP
 H. PVDC COATED CO-EX OPP
 I. WAX PAPER/GLASSINE

PPPI 008495

Table 2
Rating Based on Permeability Values at 73°F and 8RH

Film	Methyl Ethyl Ketone	Ethyl Acetate	Methyl Salicylate	Ethyl Phenyl Acetate	Limonene	B-Pinene	Toluene	Styrene	Menthol
A	G	E	G	F	G	F	E	E	E
B	F	F	G	E	E	G	G	F	E
C	F	E	E	E	E	E	E	G	E
D	G	E	E	E	E	E	E	E	E
E	F	E	E	E	E	E	E	E	E
F	E	E	G	E	G	G	E	E	E
G	P	P	P	P	G	G	P	G	G
H	G	F	F	G	G	F	F	G	E
I	E	G	G	E	G	E	E	G	G

FILM KEY:

- A. HDPE/TIC/NYLON/EVA
 B. HDPE/TIE/EVON/EVA
 C. HDPE/TIE/NYLON/TIE/EVON/TIE/NYLON/TIE/NOPE
 D. HDPE/TIE/MODIFIED NYLON/TIE/NOPE
 E. NYLON/EVON/NYLON/TIE/LLOPE/TIE/LLOPE
 F. (ORIENTED) PP/TIE/EVON/TIE/PP
 G. PP/TIE/PP/TIE/PP
 H. PVDF COATED CO-EX OPP
 I. WAX PAPER/GLASSINE

E : Excellent

G : Good

F : Fair

P : Poor

PTPI 008496

Table 3

<u>Rating</u>	<u>Number</u>
E (Excellent)	4
G (Good)	3
F (Fair)	2
P (Poor)	1

PPPI 008497

Table 4

<u>Film</u>	<u>Sum for Ratings for Barrier Properties of Flexed Films</u>	<u>Rating Sum</u>
A. HDPE/TIE/NYLON/EVA	1.25 mil	29
B. HDPE/TIE/EVOH/EVA	1.25 mil	27
C. HDPE/TIE/NYLON/TIE/EVOH/TIE/NYLON/TIE/HDPE	1.40 mil	33
D. HDPE/TIE/MODIFIED NYLON/TIE/HDPE	2.20 mil	35
E. NYLON/EVOH/NYLON/TIE/LLDPE/TIE/LLDPE	3.50 mil	34
F. (ORIENTED) PP/TIE/EVOH/TIE/PP	1.00 mil	33
G. PP/TIE/PET/TIE/PP	1.00 mil	22
H. PVDC COATED CO-EX OPP	1.80 mil	24
I. Wax Paper/Glassine		31 (unflexed)

PPPI 008498

TAB D
TO EXHIBIT 14

D

postage paid
and additional
offices

2 March-April 1987
Volume 52, No. 2

Coder: JFDAZ 52(2):245-516 (1987)
ISSN: 0022-1947

JOURNAL OF FOOD SCIENCE

Basic Research, Applied Science and Engineering

- 265 Flavor constituents of beef as influenced by forage- and grain-feeding—D.K. Larick, H.B. Hedrick, M.E. Bailey, J.E. Williams, D.L. Hancock, G.B. Garner & R.E. Morrow
- 272 Binding, sensory and storage properties of alginate-calcium structured beef steaks—W.J. Means, A.D. Clarke, J.N. Santos & G.R. Schmidt
- 257 Potassium sorbate inhibition of microorganisms growing on refrigerated packaged beef—M.C. Zamora & N.E. Zaritzky
- 263 Effects of boning time, mechanical tenderization and partial replacement of sodium chloride on the quality and microflora of boneless dry-cured ham—F.W. Leak, J.D. Kemp, J.D. Fox & B.E. Langlois
- 267 Microstructural comparisons of meat emulsions prepared with corn protein emulsified and unemulsified fat—C.S. Lin & J.F. Zayas
- 271 Functionality of six nonmeat proteins in meat emulsion systems—L.L. Parks & J.A. Carpenter
- 275 Influence of polyphosphate on storage stability of restructured beef and pork nuggets—D.L. Huffman, C.F. Ande, J.C. Corlray, M.H. Stanley & W.R. Egbert
- 279 Palatability and storage characteristics of precooked pork roasts—S.L. Jones, T.R. Carr & F.K. McKelth
- 282 Restructured mutton roast quality—V.S.S. Prasad, R.A. Field, C.J. Miller, J.C. Williams & M.L. Riley
- 286 Influence of marinating on weight gain and coating characteristics of broiler drumsticks—V.A. Proctor & F.E. Cunningham
- 290 Effect of fragmentation method and formulation on the quality of patties made from restructured spent layer meat—R. Hollender, J.H. MacNeil & M.C. Mast
- 294 Lipid peroxidation and phospholipid hydrolysis in fish muscle microsomes and frozen fish—T.J. Han & J. Ustun
- 297 Influence of frozen storage and phosphate predeposits on coating adhesion in breaded fish portions—M.L. Corey, D.L. Gerdes & R.M. Grodner
- 300 Prediction of shelf-life of frozen minced fish in terms of oxidative rancidity as measured by TBARS number—S.A. Kurade & J.D. Baranowski
- 303 Assessment of cheddar cheese quality by chromatographic analysis of free amino acids and biogenic amines—L.C. Laleye, R.E. Simard, C. Gosselin, B.H. Lee & R.N. Giroux
- 308 Mass transfer during ripening of cuanirolo Argentinian cheese—J.A. Luna & J.A. Bressan
- 312 Effect of HTST pasteurization of milk, cheese whey and cheese whey UF retentate upon the composition, physicochemical and functional properties of whey protein concentrates—C.V. Morr
- 318 Flow properties of tomato concentrates: Effect of serum viscosity and pulp content—T. Somrithichai & M.A. Rao
- 322 Effect of corn varieties on ogi quality—J.A. Adeyemi, A.T. Osunsami & M.A.B. Fakorede
- 325 *In vitro* digestibility of phytate-reduced and phenolics-reduced soy protein isolates—M.A. Riter, C.V. Morr & R.L. Thomas
- 328 c4-Heptenal: An influential volatile compound in boiled potato flavor—D.B. Josephson & R.C. Lindsay
- 332 Determination of phenolic compounds of dry beans using vanillin, redox and precipitation assays—S.S. Deshpande & M. Cheryan
- 335 Emulsifying properties of pea globulins as related to their adsorption behaviors—C. Dagorn-Scaviner, J. Gueguen & J. Lefebvre
- 342 Air drying characteristics of apricots—E.H. Abdelhaq & T.P. Labuza
- 346 Effect of pH, certain chemicals and holding time-temperature on the color of lowbush blueberry puree—C.S.T. Yang & P.P.A. Yang
- 348 Sensory techniques for measuring differences in California navel oranges treated with doses of gamma-radiation below 0.6 Kgray—M. O'Mahony & L. Goldstein
- 353 Volatile flavor components in the headspace of the Australian or "Bowen" mango—J.P. Bartley & A. Schwede
- 356 Measurement of papaya maturity by delayed light emission—W.R. Forbus Jr., S.D. Senter & H.T. Chan Jr.
- 361 Quality of fresh-market peaches within the postharvest handling system—R.L. Shewfelt, S.C. Meyers, S.E. Prussia & J.L. Jordan
- 365 A shelflife evaluation of an oriented polyethylene terephthalate package for use with hot filled apple juice—M.R. McLellan, L.R. Lind & R.W. Kime
- 369 Fouling and flux restoration of ultrafiltration of passion fruit juice—B.H. Chiang & Z.R. Yu
- 372 The contributing effect of apple pectin on the freezing point depression of apple juice concentrates—A.F. Hoo & M.R. McLellan
- 375 Clarification of apple juice by hollow fiber ultrafiltration: Fluxes and retention of odor-active volatiles—M.A. Rao, T.E. Acree, H.J. Cooley & R.W. Ennis
- 378 Effect of assay temperature on activity of citrus pectinesterase in fresh orange juice—L. Wicker, R.J. Braddock & M. Vassallo
- 381 Preparation and storage of 72°Brix orange juice concentrate—P.C. Crandall, C.S. Chen & K.C. Davis
- 386 Use of sulfur dioxide in winemaking—C.S. Ough & E.A. Crowell
- 389 Ethanol stability of casein solutions as related to storage stability of dairy-based alcoholic beverages—W.J. Donnelly

A PUBLICATION OF
THE INSTITUTE OF FOOD TECHNOLOGISTS

PPPI 008452

DTX0217

March-April 1987
Volume 52, No. 2

JOURNAL OF FOOD SCIENCE

ISSN:0022-1147

Scientific Editor Aaron E. Wasserman USDA-Philadelphia	Director of Publications John B. Kins	Board of Editors R. Berry (87) G. Carman (87) P. Carrood (87) M. Glicksman (87) D. Knorr (87) G. Ranhotra (87) J. Sink (87)	J.B. Fox (88) D.Y.C. Fung (88) M. Peleg (88) K.S. Rhee (88) L. Rockland (88) L.U. Thompson (88) J.A. Troller (88)	F. Crandall (89) B. D'Appolonia (89) H. Hultin (89) I. Ketz (89) W. Shipe (89) R. Singh (89) F. Wolfe (89)
Associate Scientific Editors Stanley J. Kazeniece Anna May Schenck	Publisher Calvert L. Willey	Managing Editor Bernie Schukraft		

• **MANUSCRIPTS** (3 copies) should be submitted to:

Dr. Aaron E. Wasserman
IFT Scientific Editor
P.O. Box 5197
Philadelphia, PA 19115

NO RESPONSIBILITY is assumed by the Institute of Food Technologists for statements and opinions expressed by the contributors to its publications.

MANUSCRIPTS should conform to the style used in *Journal of Food Science* and authors are urged to consult the "IFT Style Guide for Research Papers" (see next paragraph for availability). *Journal of Food Science* reserves the privilege of editing manuscripts to make them conform with the adopted style of the journal or returning them to authors for revision. Editing changes may be reviewed by authors before publication.

• **STYLE GUIDE:** The "IFT Style Guide for Research Papers" is published annually in *Journal of Food Science* (last date of publication: September-October, 1985, Vol. 51, No. 5, pp. 1389-1392). Copies are also available from IFT's Director of Publications.

• **PAGE CHARGES** for Publications. The IFT Executive Committee has established a page charge of \$50 per printed page for all papers published in *Journal of Food Science*. The page charge shall not constitute a bar to acceptance of research manuscripts because the author is unable to pay the charge.

• **SUBSCRIPTIONS:** All communications related to handling of subscriptions, including loss, claims, change of address, and orders for back issues should be sent to:

Subscription Department
Institute of Food Technologists
221 N. LaSalle Street, Suite 300
Chicago, IL 60601 USA

Member Subscriptions—\$15 per year.

Non-Member Subscriptions—Accepted only on a calendar year basis—no refunds. Rates include postage. Payment must accompany order. Domestic, Canada, and Mexico—\$60, all other destinations—\$70. Reduced rates for 2- and 3-year subscriptions.

Change of address notice, with old address label, is required 8 weeks before issue date.

Claims for lost copies are allowed only if received within one month after publication (3 months for foreign subscribers).

Single copies and available back issues, \$10 each postpaid; remittance to accompany order.

• **REPRINTS:** Single reprints are not available from *Journal of Food Science*. Address requests for single reprints to authors, whose addresses are found with each article. Original size and/or microform copies of individual articles, or issues, or entire volumes may be purchased from University Microfilms International, 300 N. Zeeb Road, Ann Arbor, MI 48106, U.S.A., or Dept. F.A., 30-32 Mortimer St., Dept. P.R., London W1N 7RA, England.

Quantity reprints can be ordered from IFT Publications Department—minimum of 100 copies. Price schedule available upon request.

©Copyright 1987 by Institute of Food Technologists. All rights reserved. *JOURNAL OF FOOD SCIENCE* (formerly *Food Research*) is published six times a year (bimonthly) by Institute of Food Technologists, 221 N. LaSalle Street, Chicago, IL 60601 USA. Printed in USA. Second class postage paid at Chicago, Illinois and at additional mailing offices. POSTMASTER: Send address changes to *Journal of Food Science*, 221 N. LaSalle St., Suite 300, Chicago, IL 60601.

PPPI 008453

NOTICE: This material may be protected by copyright law (Title 17 U.S. Code)

Odor Barrier Properties of Multi-Layer Packaging Films at Different Relative Humidities

E. HATZIDIMITRIU, S. G. GILBERT, and G. LOUKAKIS

ABSTRACT

A permeation cell method was developed for the determination of transmission rates of organic vapors through flexible packaging materials. The permeation rates at 23°C of some compounds for several composite films at 0% and 75% relative humidity (RH) indicated that the polyethylene vinyl alcohol and nylon combinations exhibited superior barrier properties even at elevated RH, provided that moisture barrier films were present in the laminate construction.

INTRODUCTION

THE EXPANDING USE of plastics in packaging applications competing with glass and metal puts great emphasis on the high barrier properties of the involved materials against moisture and gases (Allison, 1985) to assure an acceptable shelf life of a packaged product.

The permeation of packaging materials to odorous vapors is of significant importance, either to protect the contents against contamination from foreign odors or to retain favorable volatile flavors. Although the permeation rates of permanent gases and water vapor through many plastics have been obtained, there is a deficiency of data for permeation of organic vapors (Zobel, 1985).

The object of this study was to develop a method for quantitative evaluation of the aroma barrier of packaging materials. A series of flexible plastic films of various compositions were then tested for their permeability to some flavoring and malodorous compounds.

MATERIALS & METHODS

THE METHOD is based on the Gilbert-Pegaz permeation cell (Gilbert and Pegaz, 1969). As Fig. 1 indicates, the cell can accommodate simultaneously two films by clamping each between aluminum devices to form a pair of outer chambers and a single inner one (Gilbert et al., 1983). The devices are equipped with Viton O-rings to assure good seal between the films and the surroundings. Chambers on either side of the film have valves for inlet and outlet of permeant supply and septa for sampling.

Nitrogen is bubbled through the liquid permeant and then passed with the permeant vapors through either the middle chamber or the lower and upper compartments. Thus either one cell can be used for duplicates or in the case of very good barriers, the exposed area can be doubled. The nitrogen stream carrying the permeant vapors can be mixed before the cell with either dry or wet nitrogen to adjust the permeant final concentration or the relative humidity of the high concentration chamber. In the case of permeants with very low vapor pressure at ambient temperature, a small amount can be placed in an aluminum dish on the bottom of the cell. If adjustment of the humidity is desired, another dish with an aqueous saturated salt solution can also be placed on the bottom (Fig. 2).

The tested films appear in Table 1 with their respective compositions and thicknesses. Each film was Gelbo flexed (ASTM, 1982) for 20 cycles prior to testing to simulate severe abuse which may be encountered in packaging and distribution. All films to be exposed to a 75% RH environment at 23°C were kept for a period of 2 wk in a

desiccator over saturated sodium chloride solution. Then they were tested with the permeant vapor stream combined with controlled humidity nitrogen to provide the elevated humidity level during testing. The permeants used for the tests are also given in Table 1.

The concentrations of the permeating vapors and related humidity were monitored by gas chromatography with removal of small aliquots

Table 1—Films used for the permeation studies

- | | |
|---|--|
| A. 1.25 MI HDPE/TE/NYLON/EVA | |
| B. 1.25 MI HDPE/TE/EVOH/EVA | |
| C. 1.40 MI HDPE/TE/NYLON/EVOH/NYLON/TE/HDPE | |
| D. 2.20 MI HDPE/TE/MODIFIED/NYLON/TE/HDPE | |
| E. 1.0 MI (orientad) PP/TE/EVOH/TE/PP | |
| F. 1.0 MI PP/TE/PET-G/TE/PP | |
| G. 1.8 MI PVDC coated co-ex OPP | |

Where: HDPE	= High density polyethylene
TE	= Adhesive layer
NYLON	= Nylon 6
EVA	= Polyethylene vinyl acetate
EVOH	= Polyethylene vinyl alcohol
Modified NYLON	= Mineral filled nylon-6
PP	= Polypropylene
PET-G	= Polyethylene terephthalate-glycol
PVDC	= Polyvinylidene chloride
OPP	= Oriented polypropylene

Permeants used for the test

- | | |
|------------------|-------------------------|
| 1. Ethyl acetate | 4. Limonene |
| 2. Toluene | 5. beta-Pinene |
| 3. Styrene | 6. Ethyl phenyl acetate |

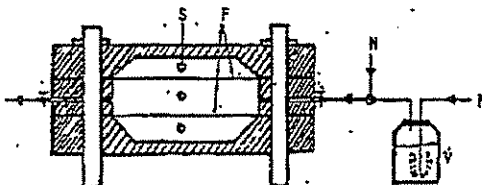


Fig. 1—Permeation cell arrangement for high vapor pressure permeants: (N) Nitrogen inlet; (V) Glass vial containing liquid permeant; (F) Film sample; (S) Septa for sampling.

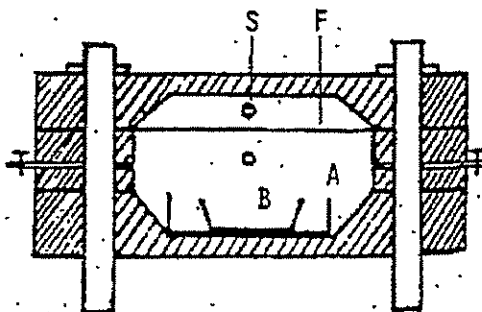


Fig. 2—Permeation cell arrangement for low vapor permeants: (A) Dish with aqueous saturated salt solution; (B) Dish with permeant; (F) Film sample; (S) Septa for sampling.

The authors are with the Dept. of Food Science, Cook College, New Jersey Agricultural Experiment Station, Rutgers Univ., New Brunswick, NJ 08903.

Film
A
B
C
D
E
F
G

Film
A
B
C
D
E
F
G

using a gas monitored curve. The in combis permeant c of permeant However semicrystall permeation ing a lag p after a test nificant per in this case of the gas film.

While a permeation pressure of crant all fi ration for l of permeant especially

THE CAL permeant . 75% RH, to 100 ppx ference ac from Table It should t to a unit d of relative vapor cont the vapor .

At 0% F exhibited t 3). The ny the HDPE permeable the least b acetate and

For the almost equ certain per beta-pinene to styrene, barrier to modified n ance can l

in they were
controlled in
ring testing
1.
red humidity
small aliquots

ylene

cerene
ketohol
6

thalate-glycol
ride
ene

ene
ene
henyl acetate

or pressure
lining liquid
7.

permeants:
sh with per-

Table 2—Permeation Rates, 0% RH, 23°C (g/m²-day-100 ppm)

Film	Ethyl acetate	Toluene	Styrene	Limonene	B-Pinene	Ethyl phenyl acetate
A	<0.003	0.001	<0.003	0.0405	0.0120	0.0085
B	0.30	0.027	0.0510	0.0012	0.0013	<0.0050
C	<0.0004	0.002	0.0054	0.0014	<0.0004	<0.0050
D	<0.0004	0.001	<0.0003	0.0018	<0.0011	<0.0050
E	<0.0004	0.0003	<0.0002	0.0400	<0.0038	<0.0070
F	6.85	1.310	0.0018	0.0315	0.0088	0.234
G	0.52	0.470	0.0046	0.0400	0.0320	0.018

Table 3—Permeation Rates, 75% RH, 23°C (g/m²-day-100 ppm)

Film	Ethyl acetate	Toluene	Styrene	Limonene	B-Pinene	Ethyl phenyl acetate
A	0.0632	0.0159	0.0120	0.0009	0.0013	0.0053
B	0.0034	0.0050	0.0037	0.0037	0.0001	<0.002
C	0.0041	0.0088	0.0059	<0.0003	0.0049	<0.002
D	0.0066	0.0006	0.0048	0.0078	0.0020	0.0076
E	0.0092	0.0034	0.0338	0.0081	0.0031	0.0061
F	0.0040	0.0020	0.0096	0.0071	too fast	0.0071
G	0.0095	0.0007	0.0051	0.0050	0.1419	0.0060

using a gas tight syringe (Gilbert and Pegaz, 1969). The plot of the moisture concentration versus sampling time gives the permeation curve. The slope of the steady state portion was determined and used in combination with the chamber volume, exposed film surface and permeant concentration difference across the film for the calculation of permeation rate in appropriate units.

However, for amorphous polymers, often found with glassy and semicrystalline polymers (Crank and Park, 1968), when the obtained permeation curves did not show a constant or steady state rate following a lag phase, the linear portion of the permeation curve was used after a testing period of two weeks. With very good barriers no significant permeating amount could be detected for certain permeants. In this case the rate was expressed as a value below the detection limit of the gas chromatograph for the permeant driving force across the film.

While a normalized driving force was used in the calculation of the permeation coefficient, the actual driving force depended on the vapor pressure of the permeant at the test temperature. For a specific permeant all films were tested at the same vapor driving force concentration for both relative humidities. Linear concentration dependence of permeation rate was assumed, although this might not be the case, especially with organic vapors (Zobel, 1985).

RESULTS & DISCUSSION

THE CALCULATED PERMEATION rates for each film and permeant are given in Table 2 for 0% RH, and Table 3 for 75% RH, respectively. The indicated values were normalized to 100 ppm (g permeant/cc of air) permeant concentration difference across the film. For comparison purposes the values from Tables 2 and 3 are presented in Fig. 3 and 4, respectively. It should be emphasized that normalizing the permeation rate to a unit driving force concentration, allows for a comparison of relative barrier properties of the tested films at only one vapor concentration. However this relationship may change as the vapor concentration is changed.

At 0% RH the nylon-EVOH and modified nylon 6 structures exhibited the best barrier properties for all the permeants (Fig. 3). The nylon-6 and both EVOH films followed next although the HDPE/EVOH/EVA combination was significantly more permeable to ethyl acetate. The PET and PVDC structures had the least barrier performance at 0% RH, especially for ethyl acetate and toluene, with PET much more inferior than PVDC.

For the 75% RH environment all the tested films exhibited almost equivalent barrier properties, with some exceptions for certain permeants. PET and PVDC were very permeable to beta-pinene. Also, the PP/EVOH/PP film appeared sensitive to styrene, and the HDPE/nylon 6/EVA structure had a lower barrier to ethyl acetate and toluene compared to EVOH and modified nylon. Overall at 75% RH the best barrier performance can be attributed to nylon 6/EVOH, modified nylon-6

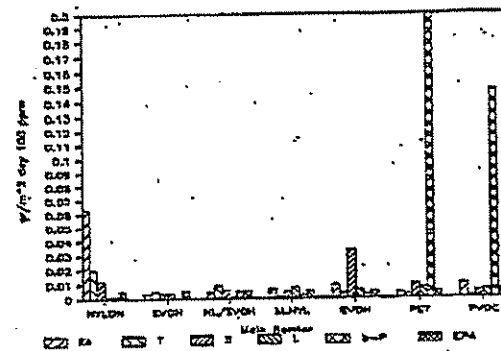


Fig. 3—Permeation rates at 0% RH, 23°C EA:ethyl acetate, T:toluene, S:styrene, L:limonene, B-P:beta pinene, EPA:ethyl phenyl acetate.

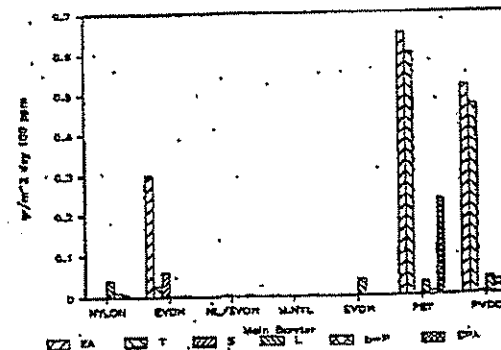


Fig. 4—Permeation rates at 75% RH, 23°C EA:ethyl acetate, T:toluene, S:styrene, L:limonene, B-P:beta pinene, EPA:ethyl phenyl acetate.

Table 4—Ethyl Acetate Permeation Tests, 23°C, 95% RH

Film	Lag time (hr)	Permeation rate (g/m ² -day-100 ppm)
A	5.6	0.247
B	24.2	0.021

PPPI 008455

ODOR BARRIER PROPS OF PACKAGING MATERIALS.

and both EVOH combinations. The HDPE/nylon 6 EVA film lost its excellent barrier properties at this RH level probably due to moisture sorption from the polyamide.

Although polyethylene vinyl alcohol (EVOH) also sorbed water, the resulting structure change at the 75% RH did not affect the permeation as much as in nylon-6. A similar difference was observed with polyvinyl alcohol and nylon-6 films for carbon dioxide and oxygen permeation (Ito, 1961; Meyer et al., 1957; Toyoshima, 1973). At 75% RH, polyvinyl alcohol was a better barrier than nylon-6 for the above gases. However, the opposite was true at 93% RH. This could be attributed to higher water sorption by polyvinyl alcohol at 93%, possibly because of a more disrupted structure for the polymer compared to nylon 6.

To determine whether EVOH, despite its ethylene content, would exhibit a similar barrier change at 93% RH as polyvinyl alcohol, when compared to nylon-6, the films HDPE/nylon 6/EVA and HDPE/EVOH/EVA were tested at 93% RH for ethyl acetate permeation. The test results are given in Table 4. The permeation rate at the steady state for nylon-6 was about twelve times faster than for EVOH. This did not agree with what was observed for permanent gases and can be attributed to the ethylene content (about 35% w/w) of EVOH. The ethylene modified the polymer structure so it was not disrupted by water sorption as much as in polyvinyl alcohol.

The lag-time, which is related to the diffusivity through the film (Crank and Park, 1968), was about four times slower for nylon-6 versus EVOH (Table 4). This indicated that ethyl acetate could diffuse four times faster in nylon 6 than in EVOH at 90% RH.

CONCLUSIONS

The nylon and polyethylene vinyl alcohol (EVOH) laminations at 0% RH appeared to have the best barrier performance which was superior to the polyethylene terephthalate-glycol (PET-G) and polyvinylidene chloride (PVDC) laminations.

A similar trend was observed even at the 75% RH level, where the water sensitive nylon and EVOH seemed to be generally well protected by the outer hydrophobic laminates. Thus the nylon and EVOH combinations maintained a superior barrier performance compared to PET-G and PVDC.

The determined barrier properties of the tested films could help in designing packaging materials which could offer better aroma protection and consequently contribute to qualitative and quantitative shelf life improvement.

REFERENCES

- Allison, H.L. 1985. High-barrier packaging materials-What are the options? Packaging March, 25.
ASTM. 1982. Film durability of flexible barrier materials. In "Annual Book of ASTM Standards," Vol. 21, p. 414. American Society for Testing and Materials, Philadelphia, PA.
Crank, J. and Park, G.S. 1968. Methods of measurement. Ch. 1. In "Diffusion in Polymers," J. Crank and G.S. Park (Ed.), p. 1. Academic Press, New York.
Gilbert, S.G., Batzidimitris, E., Lai, C., and Panny, N. 1983. Study of barrier properties of polymeric films to various organic aromatic vapors. In "Instrumental Analysis of Foods," G. Charnamborn and G. Inglet (Ed.), Vol. 1, p. 405. Academic Press, New York.
Gilbert, S.G. and Pagan, D. 1988. Find new way to measure gas permeability. Packaging Jan. 68.
Ito, Y. 1961. Permeability of measuring high-polymer films. Kobunshi Kagaku 18: 153.
Meyer, J.A., Rogers, C.E., Stannett, V., and Szwarc, M. 1957. Studies in the gas and vapor permeability of plastic films and coated papers. *Appl* 40: 142.
Toyoshima, K. 1973. Properties of polyvinyl alcohol films. Ch. 14 in "Polyvinyl Alcohol," C.A. Finch (Ed.), p. 339. John Wiley & Sons, New York.
Zobel, M.G.R. 1985. The odor permeability of polypropylene packaging film. *Polymer Testing* 5: 153.
Ms received 6/11/86; revised 10/30/86; accepted 11/28/86.

This work was performed as a part of NIAES Project No. D-10533-1-86 supported by the N.J. Agricultural Experiment Station.

A paper of the Journal Series, N.J. Agricultural Experiment Station, Cook College, Rutgers, The State University, Department of Food Science, New Brunswick, NJ 08903. This work was performed as a part of NIAES Project No. D-10533-1-86, supported by the N.J. Agricultural Experiment Station.

MODIFICATION OF GELATIN BY IMMOBILIZED PROTEASE. From page 468

proteases of different specificities is now being tested to further improve the present data.

REFERENCES

- Picler, R. 1972. The rapid determination of amino groups with TNBS. In "Methods in Enzymology," Vol. 25, p. 464. Academic Press, New York.
Pinch, C.A. and Jelling, A. 1977. Physical properties of gelatin. In "The Science and Technology of Gelatin," p. 250. Academic Press, New York.
Hinterwiesinger, R. 1977. Technology of gelatin manufacture. In "The Science and Technology of Gelatin," p. 315. Academic Press, New York.
Johns, N.B. 1977. Uses of gelatin in edible products. In "The Science and Technology of Gelatin," p. 368. Academic Press, New York.
Johns, F. and Courts, A. 1977. Relationship between collagen and gelatin. In "The Science and Technology of Gelatin," p. 138. Academic Press, New York.
Kunitz, M. 1947. Crystalline soybean trypsin inhibitor. II. General properties. *J. Gen. Physiol.* 30: 291.
Moore, S. and Szabo, R.H. 1954. A modified ninhydrin reagent for the photometric determination of amino acid and related compounds. *J. Biol. Chem.* 211: 907.

- Moriwaka, K., Oka, T., and Tsuruki, H. 1970. Subtilisin BPN: Kinetic study with oligopeptides. *Arch. Biochem. Biophys.* 138: 518.
Nishio, T. and Hayaishi, R. 1984. Digestion of protein substrates by subtilisin immobilization changes the pattern of products. *Arch. Biochem. Biophys.* 229: 304.
Nishio, T. and Hayaishi, R. 1985. Regeneration of a collagen-like circular dichroism spectrum from industrial gelatin. *Agric. Biol. Chem.* 49: 1675.
Nishio, T., Scheraga, N.M., Reynolds, J.A., and Tanford, C. 1976. Use of gel chromatography for the determination of the Stokes radii of proteins in the presence and absence of detergents. A reexamination. *Biochemistry* 15: 3884.
Westall, H.H. 1978. Covalent coupling methods for inorganic support materials. In "Methods in Enzymology," Vol. 44, p. 134. Academic Press, New York.
Ms received 5/18/86; revised 9/15/86; accepted 10/9/86.

We are grateful to Mr. N. Ito of the Technical Section of the Gelatin Division of Nitta Gelatin Co. Ltd. for measurement of the molecular weights of gelatins and to Mr. S. Taniguchi and Mr. K. Suzuki of the Research Laboratory of Nitta Gelatin Co. Ltd. for encouragement and discussion throughout this study.

Autoxidized
droperoxide (interactions c
was antioxi
bound to cas
SP and LAH
and made ca
gestible dur
incubation w
acids end to

POLYUNS.
oxygen to it
The peroxid
various oxi
termed sec
teriation a
These autox
decreased b
1976; Chan
with peroxi
residues wa
1975a) and
cushita, 197
ids with pr
lysozyme in
and Karel, I
of interacti
undergoing
In this su
roxide (LAI
and digestib

Materials

Casins acc
Co., Inc. (U
was diluted w
activity of 15
days. LA, L
dried LA by
sawa et al.,
> 89%, resp
polymers, 26
monomeric ac

Authors Kai
Agricultural
with the De
School of St
657, Japan.

PPPI 008456

TAB E
TO EXHIBIT 14

SPEECH

SLIDE 1
Good Morning Ladies and Gentlemen. My name is Earl Hatley and I'm with the Allied Corporation in the Engineered Plastics Division. I want to thank the Society of Plastic Engineers Chicago Section for inviting me here this afternoon to speak to you regarding nylon and its various performance properties. In fact, the name of my paper is "The Performance of Nylon Particularly as a Flavor Aroma and Odor Barrier".

As some of you may be aware Allied Corporation entered into a flavor and aroma barrier study with Dr. Seymour Gilbert at the Rutgers University approximately three years ago. We initiated the study with Dr. Gilbert because at the time there was much discussion in the trade regarding flavor and aroma barriers but there was no empirical data available to substantiate what many felt was taking place. Several of our customer converters had done very preliminary type testing and had gotten an indication that nylon was a very effective flavor aroma and odor barrier. However, there was no objective knowledge such as you would obtain from an university study.

Allied commissioned Rutgers University to study and compare the flavor and aroma barrier properties of commercially available packaging materials with common organic compounds associated with food ingredients and laminated materials used for food packaging.

The film materials tested included nylon, polyvinylidene chloride (PVDC), ethyl vinyl alcohol (EVOH), and glassine. Those

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

PPPI 014276

DTX0002

-2-

results indicated that nylon provided good to excellent protection against the permeation of flavors and aromas and offers one of the most economical barriers per mil thickness.

SLIDE 2
Properties I might add that nylon also provides excellent grease and oil resistance in high temperature performance as well as impact, puncture, and tear resistant properties. The study indicated that coextruded films with thin nylon cores proved to have the broadest range of performance properties of the films tested with optimum flavor aroma barrier.

SLIDE 3
TEST
CONDITIONS This first Rutgers study represented the first time that data had been compiled for specific permeants that affect flavor and aroma barriers of packaged foods. The testing procedure involved the use of a special permeation cell developed by Dr. Gilbert. Test films were pre-conditioned and aged for ten days at 70°F and 100% relative humidity and Gelboflexed for 20 times to simulate shipping and handling conditions.

SLIDE 4
Definition In the first and second studies, film samples were clamped in the permeation cell and test compounds ^{OF} and concentrations of 100 parts per million were introduced to chambers within the cell. At intervals the concentrations of test compounds in the chambers were measured by gas chromatograph to determine the permeation rate of the compounds. The items tests included allyl sulfide
SLIDE 5
(oil of garlic) and acetic acid (vinegar); methyl ethyl ketone
(cell) and ethyl acetate (solvents used in food packaging); and toluene
(aromatic chemical used to simulate automobile and truck
SLIDE 6
exhaust).
Kagiam

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

PPPI 014277

-3-

SLIDE 7
A special note there was one deviation on the test method which had to be used for ethyl phenol acetate. Due to the low vapor pressure of this permeant at 73°F only one film sample was used per permeation cell according to Dr. Gilbert. An aluminum weighing dish containing the permeant was placed on the bottom of each cell. Then the film was placed above the dish and clamped between the upper and lower compartments of the cell. Thus, the upper part was a low concentration side while the lower one was saturated with vapors of the permeant.

SLIDE 8
3 LFNK
1st study
In this first study the nylon film coextrusion outperformed the other film structures tested with the exception of the ones including EVOH, which proved a better permeation resistance to acetic acid, ethyl acetate and toluene. In all instances, however, the performance of nylon film proved acceptability compared with EVOH which, as you may know, is probably twice the cost of nylon in resin form.

As some of you may be aware nylon and EVOH are used together in film structures sandwiched as core layers between layers of high density polyethylene or other polyolefins, for moisture protection, to provide extremely functional specifications especially in the area of thermoforming applications where EVOH has provided the oxygen barrier and nylon also the oxygen barrier but more importantly nylon gives it the strength for thermoforming without flex cracking. In these specifications nylon forms an inseparable bond with EVOH protecting the more sensitive EVOH

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

PPPI 014278

-4-

from heat degradation and flex cracking and may serve as a moisture absorber according to some of our clients. Both nylon and EVOH have excellent oxygen barriers.

21069
EJECTIVE Do to the results of the first Rutgers study, which indicated that both nylon and EVOH are effective flavor and aroma barriers, we decided to commission Rutgers to do a second flavor and aroma study to determine the following objectives:

- (1) To determine whether nylon and EVOH in a single specification have a synergistic effect on flavor and aroma which becomes cost effective.
- (2) To test additional permeants which have a broader range in simulating various flavors and aromas used in food, medical, and industrial packaging, and additional polymers / structures to these permeants to test their barrier properties.
- (3) To test under 0% relative humidity as done in the first study but more importantly to also test under high relative humidity, that is 80%, to see the effects of moisture on flavor, aroma, and odor barrier properties.

The permeants which were tested in the second study were as follows:

- (1) Methyl Ethyl Ketone, a solvent.
- (2) Ethyl Acetate, a solvent.
- 210610
solvent (3) Methyl Salicylate, a permeant found in breath fresheners and other products.
- (4) Ethyl Phenol Acetate, a permeant found in soaps and products of that nature.

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

PPPI 014279

-5-

- (5) Limolene, a permeant simulating flavorant found in various confections.
- (6) Beta-pinene, a permeant found in various household cleaners.
- (7) Toluene, a solvent used to simulate various hydrocarbons especially in motor fuels, and diesel exhausts.
- (8) Styrene, a permeant used to simulate various undesirable compounds that might migrate into food stuffs through packaging or from packaging materials.
- (9) Menthol, a permeant design to simulate the types of organic compounds used not only in breath fresheners, and tobacco products but also to simulate in organic compounds used in medicinal packaging.

The packaging structures tested were those that can be commercially produced. Some of which are commercially produced others of which are developmental. Those structures were as follows:

- a) 1.25 mil coextrusion containing high density polyethylene - Tie - nylon - EVA.
- b) 1.25 mil coextrusion containing high density polyethylene - Tie - EVOH - EVA.

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

PPPI 014280

-6-

- c) 1.4 mil coextrusion containing high density polyethylene - Tie - nylon - Tie - EVOH - Tie - nylon-Tie-high density polyethylene.
- d) 2.2 mil coextrusion containing high density polyethylene - Tie - modified nylon - Tie - high density polyethylene.
- e) 3.5 mil coextrusion containing nylon - EVOH - nylon - Tie linear low density polyethylene - Tie - linear low density polyethylene.
- f) 1 mil oriented ^{FILM} polypropylene copolymer-Tie - PETG - Tie - copolymer polypropylene.
- h) 1.8 mil PVDC coated coextruded oriented polypropylene.
- i) 53 pound wax paper, 4 pounds paraffin wax - 20 pounds glassine - 7-1/2 pounds microcrystalline wax - 20 pounds glassine - 4 pounds paraffin wax.

710E12
5460

The data I am about to present were tested under the following conditions: Temperature was 73°F. Moisture 0% relative humidity. Material abuse all films except Item I were gelbolflexed 20 cycles. Film I was creased at 180° once and released to flat.

We reasoned that by creasing the 53 pounds wax paper once and releasing to flat, we were simulating as best as possible the type of abuse that this material gets by manufacturers when its folded and made into a pouch on a double package maker machine.

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

PPPI 014281

-7-

I think that perhaps we were too kind to this material because in reviewing the procedures and the way the material is handled on the machine, it is probably abused more than what we've given it.

In addition, the data that I'll be presenting to you this afternoon on the second flavor aroma study that we've done at Rutgers will be under 0% relative humidity only. The higher humidity, that is under 80% relative humidity, on the same structures is now in progress and will not be completed in November.

The tables you are about to see are all presented in permeabilities of grams per square meter per day at a permeant concentration of 100 parts per million.

As you can see from the first slide we are presenting for methyl ethyl ketone there is significant barrier properties for a number of the structures which we have tested. You'll note that for the value of .43 for the Item A which is the high density PE-nylon-EVA compared to the .65 for Item B which is the high density PE-EVOH-EVA. Those structures are very identical in makeup with only the barrier being different. That is the actual thickness of materials is about the same.

SLIDE 13
MEK

The value obtained for the coextrusion in Item C is .90. You'll note that our findings are somewhat surprising on this structure because you really don't get that much more barrier property from a combination of nylon EVOH nylon in a coextruded structure as we had hypothesized from the initial reports. The

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

PPPI 014282

-8-

values of the first three items are very similar in numerical content. When your measuring at grams per square meter per day, either one of these values is considered to be a very good barrier.

You'll notice for Item D the high density PE-modified nylon-high density PE a value of .77, again very comparable to the first three items that are presented.

This structure has a modified nylon in it whereas Item A has a straight nylon 6, Item B EVOH only and Item C a combination of nylon six and EVOH.

You'll notice for Item E the nylon EVOH nylon linear low density linear low density coextrusion at 3.5 mils. That value was .77 again very similar to the first four that are presented. We suspect that this one may not be showing quite as good as we would have expected due to the thickness and the gelboflexing. We've found thinner is better in coextrusions when gelboflexing and to simulating abuse. Several of our converter customers tell us that that is also their findings.

Item F, you'll notice that there's a very good barrier found of less than .01 for the oriented coextrusion consisting of copolymer polypropylene EVOH-copolymer polypropylene. This finding ^{quite} really substantiates the finding that we found in the first study for EVOH and MEK wherein we found a similar very good barrier for EVOH. ~~In the first study we found the value of .09 for unoriented EVOH.~~ Here were finding a value of .01 for oriented

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

PPPI 014283

-9-

Item B is unexpected
 EVOH. ~~So both values are excellent.~~ It's questionable here whether the addition of orientation provides that much more barrier for the money. Of course, when you orient you'd be doing that to obtain additional properties for your purpose.

Item G, the coextrusion containing polypropylene PETG polypropylene. You notice there's a very poor finding of 2.4 grams for methyl ethyl ketone permeant passing through the PETG. Dr. Gilbert had indicated to us that he expected this type of finding and so we were not surprised that the PETG proved to have a very poor functional barrier for solvents.

Item H is the 1.8 mil PVDC coated coextruded oriented polypropylene with a barrier of .44 for methyl ethyl ketone. This has proved to be a fairly good barrier in this study, however, in the first study we tested a different type of PVDC polypropylene and for MEK we got a barrier of 3 grams. The second film is thicker, the orientation may be different, and there's a different PVDC. These films are from different manufacturers.

Item I which is the 53 pound wax paper, you note has the best barrier of any of the structures at .02 for MEK. The large food processing manufacturer who supplied this material to us did indicate that their own test had showed that it was a pretty good barrier for some permeants.

QDE 14
E.A The next slide we want to present is that of ethyl acetate as a permeant simulating solvents used in food packaging and also

CONFIDENTIAL SUBJECT
 TO PROTECTIVE ORDER

PPPI 014284

-10-

represent some flavorants in food processing. You'll notice from the slide that the first six items all represent a very good barrier. They're all fairly equal with slight differences in the value. However for Item G, which is the coextruded polypropylene PETG polypropylene structure, its not a very good barrier for ethyl acetate, fully 6.86 grams going through that structure under dry conditions and I don't think you'd want to chose that to protect your product if it were in a lamination where they're using ethyl acetate as a solvent to cut adhesives etc. The remaining two items, the PVDC coated coextruded polypropylene-a good barrier, and last but not least the 53 pound wax paper-an excellent barrier for ethyl acetate at .04 grams. Dr. Gilbert indicates that ethyl acetate will also simulate a banana type aroma. Here, there are at least eight of the structures that may be contenders for that type of barrier packaging.

LIDE 15 The next slide we want to present is for menthol salicylate. You'll notice that for the first six structures there is a very good barrier found for this permeant. As you may recall you've seen this used in breath fresheners and that type of product as well as others. However, again in Item G which is the coextruded polypropylene PETG polypropylene, the barrier is not very desirable, 2.16 grams per square meter. To review we have found for methyl ethyl ketone, ethyl acetate and menthol salicytate, that PETG is not a very effective barrier if you were to consider using PETG in a coextrusion.

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

PPPI 014285

-11-

Notice structure H, .87 grams not as good as the other barriers involved, in fact, it is significantly lesser of a barrier for the menthol salicylate than either of the first six items.

Item I, the 53 pound wax paper again makes a very good showing as far as a barrier property for menthol salicylate at .024 grams.

2/15/6 The next slide we'll present is on ethyl phenol acetate a permeant which is used to simulate the type of aromas we find in soaps, etc.

You'll note for the first six structures that the barriers are just about equal for ethyl phenol acetate. As I have mentioned in my earlier remarks for methyl ethyl ketone, this permeant also demonstrates that there really is not that much of a synergistic effect in terms of combining nylon and EVOH in a packaging structure to gain an even better barrier than you would by specifying either nylon by itself or either EVOH by itself in a packaging structure. Of course if you combine nylon and EVOH in a structure you may be doing that to get a super oxygen barrier one of which you would not be able to obtain with the nylon by itself.

The value obtained for phenol ethyl acetate for Item G, the PETG coextrusion is significantly not as good as the first six items. Item H, the PVDC coated oriented polypropylene makes a good showing at .016 grams. Item I, the 53 pound wax paper is

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

PPPI 014286

-12-

good odor structure at .008 grams per square meter for the permeant.

SLIDE 17

The next slide is for limonene, a permeant used to simulate the lemon flavor. You'll note for the values we have expressed for the first six coextrusions incorporating nylon by itself, EVOH by itself, combinations of nylon and EVOH, modified nylon, and the orientation effect; that the barriers are pretty much comparable for each of these items. Structure G which has not made a good showing in previous permeants does comparably to the first six structures with a .03 value as does Structure H which is the PVDC coated oriented polypropylene, and Structure I - 53 pound wax paper. All nine structures prove to be a good barriers for the limonene.

SLIDE 18

The next slide is for Beta- pinene which is used to simulate the type of odors you'd find in household cleaners. You'll notice that all nine structures are a good barrier to Beta - pinene with, some of course, being significantly better than others. For example Item C which is the nylon EVOH combination does prove to have one of the better barriers for this type of packaging. You'll note for Item H which is the PVDC coated oriented polypropylene is the least desireable of the group at .03 grams per square meter.

SLIDE 19

The next slide is for toluene. This permeant is probably the one that is most often used by food packagers to simulate the types of environmental conditions that food products are exposed to in the distribution system especially through trucking.

CONFIDENTIAL SUBJECT PPPI 014287
TO PROTECTIVE ORDER

-13-

We are first alerted to this permeant by a major confectionary manufacturer who had discovered that his products were picking up odors in transit. By testing with toluene he found it was the diesel exhaust or aromatic hydrocarbon in the exhaust that were permeating his packaging and effecting his product and staling it. He has subsequently changed his package to an intermediate structure, however, is still desiring to get a coextrusion containing nylon which will be a better barrier to toluene than the structure he is currently using.

You'll note from the slide that the first six structures that we've discussed prior do show good barrier for toluene, however, noticing Item H the PVDC coated oriented polypropylene that is significantly different at .47 than the others. This happens to be the structure I spoke about earlier. You notice that Item A which is a nylon containing coextrusion is .001 versus Item H which is .47; that difference in permeation is the manufacturer's reason he desires to change to a nylon coextrusion if he could find one that would be machinable and process in his plants. You'll notice Item G the PETG coextrusion is the most undesirable barrier structure of all for toluene.

SLIDE 20
The next slide we want to present is for styrene. You notice that for each of the structures there's a good barrier for styrene. The nylon only coextrusion, and the modified nylon coextrusion, as well as the nylon EVOH nylon 3-1/2 mil structure,

-14-

and the oriented EVOH structure all make very good showings as far as barrier for styrene. You'll notice there may be an orientation effect on the EVOH since the unoriented coextrusion with EVOH is .06 whereas the oriented coextrusion with EVOH is .0002. It's a challenge to analyze differences such as these in searching for explanations of the effects of various polymers and machining techniques for barrier properties.

LIFE 20 The next slide is for ^{MENTHOL} ~~methanol~~. All nine structures involved have an excellent barrier to ~~methanol~~ ^{MENTHOL}.

LIFE 21 *SLIDE 21* Now there is significant data presented here for you to assimilate in this short time. *SLIDE 22* Rutgers University has made up a rating system for the permeants in each of their classes. This next slide shows this rating system based on Excellent-E, Good-G, Fair-F and Poor-P. The ratings are not to be taken of one column versus another column. The ratings are only to be used on one structure versus the other structure for the permeant tested.

SLIDE 23 *SLIDE 22* Dr. Gilbert has assigned numerical values for each letter code represented by the next chart. For Excellent, he assigned a value of four (4). For Good a value of three (3), and for Fair and value of two (2) with Poor being a value of one (1). The cumulative ratings are as follows.

LIFE 23 *SLIDE 23* *SLIDE 22* You'll notice that the overall rating of the high density modified nylon high density represented by Structure D is best.

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

PPPI 014289

-15-

The modification within nylon is still in the developmental stages but suffice to say that it is extremely cost effective.

SLIDE 24
Total If you were to compare this structure versus the one represented in B which is an EVOH specification you would get an excellent barrier. Using the modified nylon would be more cost effective than if you were to use other more expensive polymers.

SLIDE 25
set effective As in our first study through Rutgers University the second study also indicates that nylon is the most cost effective barrier for flavors, aromas and odors. As mentioned earlier in the discussion, the table representing the raw data for all the permeants indicates that by combining nylon and EVOH together there is not a significant synergistic effect in terms of barrier properties compared to a nylon only containing coextrusion or an EVOH only containing coextrusion whether they be oriented or unoriented. In addition the cost effective nylon only coextrusion or the modified nylon coextrusion makes an excellent showing for all the permeants versus the PETG coextrusion and the PVDC coated oriented polypropylene film. It is noted that the 53 pound wax paper does make a very good showing as far as the barrier material is concerned. However, we are told that this material is becoming extremely costly and there are limited manufacturers these days. Also this material has limited application since it is currently used ^{ONLY IN} as liner stock for certain dry foods. It is opaque in color, does not have applicable tensile strength, impact strength, and a number of other desirable features that you would find in a plastic film.

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

PPPI 014290

-16-

We think you'll agree that the second study is very significant in terms of gathering data for those of you who are searching for a cost effective barrier to engineer for your customers or for your company if you are employed by a food, medical, or industrial company. The findings are particularly important to those of you as packagers of shelf stable foods whether your packaging baked goods, candies, confections, flavor enhanced cereals, cake mixes or snack foods which need to keep their flavors in for long periods and keep out odors and flavors during handling, shipping and storage.

We thank you for allowing us to present this to you today and we will have the balance of our information in December of 1985 for 80% relative humidity testing of the same structures.

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

PPPI 014291

Table 1:
Permeability in $\text{gr}/\text{m}^2\text{day}\times 100$ ppm at 73°F and 0.8RH

Film	Methyl Ethyl Ketone	Ethyl Acetate	Methyl Salicylate	Ethyl Phenyl Acetate	Limonene	B-Pinene	Toluene	Styrene	Menthol
A	0.43	<0.0003	0.0046	0.0085	0.0409	0.0120	0.001	<0.0003	<0.0002
B	0.65	0.30	0.0011	<0.0060	0.0012	0.0013	0.027	0.0610	<0.0001
C	0.90	<0.0004	<0.0003	<0.0080	0.0014	<0.0004	0.002	0.0054	<0.0001
D	0.65	<0.0004	<0.0002	<0.0080	0.0018	<0.0011	0.001	<0.0003	<0.0001
E	0.77	<0.0004	<0.0002	<0.0080	<0.0003	<0.0009	0.0004	0.0005	<0.0001
F	<0.01	<0.0004	0.009	<0.0070	0.0400	0.0036	0.0003	<0.0002	<0.0002
G	2.40	6.86	2.160	0.234	0.0315	0.0088	1.310	0.0018	0.0020
H	0.44	0.52	0.871	0.016	0.0400	0.0320	0.470	0.0046	<0.0002
I	0.02	0.04	0.024	<0.0080	0.0106	<0.0012	0.005	0.0059	0.0011

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

PPPI 014292

Table 2

Rating Based on Permeability Values at 73°F and 38RH

Film	Methyl Ethyl Ketone	Ethyl Acetate	Methyl Salicylate	Ethyl Phenyl Acetate	Limonene	B-Pinene	Toluene	Styrene	Menthol
A	G	E	G	F	G	F	E	E	E
B	F	F	G	E	E	G	G	F	E
C	F	E	E	E	E	E	E	G	E
D	G	E	E	E	E	E	E	E	E
E	F	E	E	E	E	E	E	E	E
F	E	E	G	E	G	G	E	E	E
G	P	P	P	P	G	G	P	G	G
H	G	F	F	G	G	F	F	G	E
I	E	G	G	E	G	E	E	G	G

E : Excellent

G : Good

F : Fair

P : Poor

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

PPPI 014293

Table 3

<u>Rating</u>	<u>Number</u>
E (Excellent)	4
G (Good)	3
F (Fair)	2
P (Poor)	1

CONFIDENTIAL SUBJECT
TO PROTECTIVE ORDER

PPPI 014294

Table 4

<u>Film</u>	<u>Sum for Ratings for Barrier Properties of flexed films</u>	<u>Rating Sum</u>
A. HDPE/NYLON/EVA	1.25 mil	29
B. HDPE/EVOH/EVA	1.25 mil	27
C. HDPE/NYLON/EVOH/NYLON/HDPE	1.40 mil	33
D. HDPE/MOD. NYLON/HDPE	2.20 mil	35
E. NYLON/EVOH/NYLON/LLDPE/LLDPE	3.50 mil	34
F. OPP/EVOH/PP	1.00 mil	33
G. PP/PET-G/PP	1.00 mil	22
H. PVDC Coated Co-Ex OPP	1.80 mil	24
I. Wax paper/Glassine		31(unflexed)

CONFIDENTIAL-SUBJECT
TO PROTECTIVE ORDER

PPPI 014295